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13. ABSTRACT (Maximum 200 words) Concentrating on the problem of fuel line fouling possible in the next generation aircraft gas turbines, extensive experimentation on the pyrolysis of the endothermic fuels, methylcyclohexane, decalin and tetraline under sub and supercritical was completed. Results revealed that the fuel decomposition rates had an activation energy essentially the same for all fuels and cases, but that the pre-exponential factor was two orders of magnitude higher under supercritical conditions. Although the pyrolysis products were generally the same, higher order cyclic hydrocarbons were found under supercritical conditions. These compounds were also found to have lead to known precursors for particulate formation and to have increased with increasing pressure. These differences between sub and supercritical conditions have been postulated to be due to the phenomenon known as caging at high pressures.				
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1998 Progress Report

FUELS COMBUSTION RESEARCH SUPERCRITICAL FUEL PYROLYSIS (AFOSR GRANT F49620-98-1-0134)

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A. Summary

Progress has continued in the investigation of the thermal and combustion characteristics of fuels at conditions of special interest to the Air Force. Recent efforts have concentrated on the characteristics of endothermic fuels necessary as coolants in next generation aircraft and fuel fouling under sub- and super-critical conditions.

B. Technical Discussion

Various hydrocarbon fuels, which can be classified as undergoing endothermic pyrolysis, are being considered for next generation aircraft of interest to the Air Force. Methycyclohexane, a prototype endothermic fuel, was the focus of the study reported last year (1,2,3). Currently reported are experiments and models for the possible candidate endothermic fuels - decalin, tetralin and n-decane. In particular, their pyrolysis characteristics under sub- and super-critical conditions were studied to determine whether their chemistry would lead to particulate formation (fouling) in fuel lines. Since they must eventually go under combustion in the engine, their gas phase reaction kinetics has been under investigation as well. Progress has been extensive and is detailed in the following paragraphs.

The supercritical decalin, tetralin, and decane pyrolysis mechanisms were investigated as a function of temperature and pressure in the high pressure plug flow reaction described in detail in previous reports. In addition, mixtures of 90% (molar) decalin with 10% decane and 90% tetralin with 10% decane were examined over a range of temperatures at a constant pressure of 3.13 MPa. Temperatures examined in each set of experiments ranged from around 700 K to 810 K. Typical pressures ranged from 0.2 to 10.0 MPa. Since the density of the reacting stream varied with temperature, pressure, and conversion, the residence time in the reactor varied.

Supercritical decalin pyrolysis was examined over a temperature range of 730 to 810 K at a pressure of 4.14 MPa. The major products of supercritical decalin pyrolysis at 810 K and a residence time of 62 seconds, listed in order of decreasing molar yield included: methane, propane, ethane, propene, ethene, butene, butane, methylhexahydroindane, and indene. The yield of products increased exponentially as temperature increased, as expected when Arrhenius kinetics predominate. A global activation energy, assuming pseudo first order reaction, of 276 ± 10 kcal/mole (Fig. 1) was determined for decalin decay from 729 to 815 K at 4.14 MPa. A pre-exponential was found to be $10^{15.8 \pm 1.5}$. This analysis did not differentiate between the cis and the trans decalin isomers but considered their sum. The pseudo first order assumption was verified in a second set of experiments which examined decalin decomposition over a range of pressures at a constant temperature of 761 K. A global reaction order of 0.98 was determined, supporting the global pseudo first-order assumption.

Supercritical tetralin pyrolysis over a range of temperatures from 702 K to 802 K at 4.77 MPa was also examined. At 802 K and a residence time of 79 sec., major products listed in order of decreasing yield included: naphthalene, methylindane, ethane, methane, ethene, phenylbutane, propane, propene, phenylpropane, ethylbenzene, and toluene. A pseudo first order global activation energy for tetralin pyrolysis was determined to be 273 kJ/mole, with a pre-exponential of $10^{15.9 \pm 1.5}$. A global reaction order of 1.01 was determined from experiments where pressure was varied at a constant temperature.

As well, in order to assess the potential application of tetralin and decalin as H-donors, supercritical pyrolysis of mixtures of 10% decane in 90% decalin and 90% tetralin (molar percent) were also examined. These experiments were conducted over a temperature range of 700 to 800 K at a pressure of 3.13 MPa. An Arrhenius plot illustrating decane decomposition in three different media is shown in Fig. 2. As Fig. 2 illustrates, pure decane decomposition has the highest decay rate observed in this temperature range. Although it has the highest activation energy, its pre-exponential factor is much greater than that found in either of the mixtures.

More recent gas phase decalin pyrolysis results (4) are reported in Fig. 3. The major pyrolysis products found included large amounts of methane, alkene (ethene, propene, butadiene) and the aromatics benzene and toluene. Major products of supercritical decalin pyrolysis at 730-810 K and 4.14 MPa included similar light alkenes (ethene, propene, butadiene) as well as some benzene and toluene, especially at higher temperatures. However, the lower temperature supercritical pyrolysis also included an abundance of light alkanes, methylhexahydroindane, indene, indane, methylenecyclohexene, and cyclohexadiene, species not found in the one atmosphere higher temperature gas phase studies.

In the same temperature range as this investigation (770 K) and at one bar, Ondruschka et al. (5) investigated gas phase decalin pyrolysis using laser powered homogeneous pyrolysis and a quartz flow reactor. At 770 K, they found an abundance of methane, ethane, ethene, propane, propene, butene, butadiene, cyclical C₅ products, benzene, and methylenecyclohexene. Again, the major light olefins and alkanes observed in their work were

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consistent with the results discussed here. Although considerable similarity was found between the results of this study and that conducted by Ondruschka et al. At 770 K, a striking contrast between the one bar and the supercritical study is found in the prevalence of methylhexahydroindane at supercritical conditions, a major product not found by Ondruschka et al., and in the relatively low yields of methylenecyclohexene in the supercritical pyrolysis. The differences in product distribution between the two studies conducted at the same temperature but different pressures indicated that the major reaction mechanisms of decalin pyrolysis may exhibit some pressure or concentration dependence.

Prior to a discussion of possible explanations for the pressure dependence of these reaction mechanisms, it is useful to consider in detail what the possible reaction pathways for some of the major products are. As shown in pathways I to III of Fig. 4, methylhexahydroindane formation is initiated by H-abstraction from any of the decalin C-H bonds. A subsequent β -scission creates a cyclohexane structure with two side chains, one olefinic, and one radical. The two side chains link by radical site addition to the double bond and, with H transfer from a neighboring molecule, methylhexahydroindane is formed. Representative β -scission pathways for alkene formation are illustrated in pathways IV and V. Methylenecyclohexene formation as proposed by Ondruschka, et al. (5) is illustrated in pathway VI. Pathway VI is initially identical to pathway II. However, immediately after the β -scission, instead of the two side chains joining as in pathway II, a 1,5 H transfer which takes advantage of the mobility of the radical side chain shifts the radical site to the other ring. Subsequent β -scission results in methylenecyclohexene.

These mechanistic pathways are revealing as to how the pressure dependence of some of the dominant decomposition pathways may be occurring. Mechanistic pressure dependence was investigated in greater detail in a second set of experiments which examined decalin pyrolysis at a constant temperature of 761 K and a range of pressures (0.3 to 8.6 MPa). The mole fraction yields of methylhexahydroindane over yields of methylenecyclohexene as pressure was found to be varied at a constant temperature of 761K. Clearly, methylenecyclohexene formation is favored at low pressure while methylhexahydroindane formation is favored at high pressures. Because these products appear to be formed from the same or similar intermediates (pathways I-III and VI), a favorable concentration dependence for the ring contraction of pathways I-III over the 1,5 H isomerization of pathway VI and other alternatives to ring contraction may explain this trend. One explanation may be caging effects, as has been proposed in a related study (6).

In the earlier study of supercritical methylcyclohexane pyrolysis (6), it was postulated that the production of methylcyclopentane structures resulted from ring condensation (C_6 to C_5) from a cyclohexenyl radical, similar to the methylhexahydroindane formation mechanism proposed here. It was suggested that ring condensation may be influenced by a physical cage of molecules surrounding the C_6 radical, a consequence of the very high concentration environment associated with supercritical fluids or liquids. The cage promotes the formation of a more compact structure, a C_5 ring, and discourages the radical from opening up to form a larger, linear structure -- such as the large radical intermediate of pathway VI of Fig. 4. Thus, caging effects promoting the ring contraction of pathways I-III and discouraging the formation of the large intermediate of pathway VI may be responsible for increasing yields of methylhexahydroindane and decreasing yields of methylenecyclohexene with increasing pressure.

In addition to being used for development of possible reaction mechanisms, the data from this set of experiments were also used to measure global kinetic parameters. The measured global activation energy of 276 kJ/mole and global pre-exponential of $10^{15.8} \text{ sec}^{-1}$ show good agreement with those found in supercritical decalin pyrolysis studies at similar temperatures and pressures. For the program's one atmosphere gas-phase studies (7), a global activation energy of 217 kJ/mole and $A=10^{11.4}$ were determined. The much lower EA in this work is thought to result from a more fully developed radical pool in the higher temperature gas phase study. A more fully developed radical pool could suggest greater participation of the very low activation energy radical abstraction reactions (typically around 10-30 kJ/mole) in the global fuel decay scheme and less participation of the higher activation energy C-C homolysis reactions (typically around 350 kJ/mole). The combination of these factors would tend to reduce EA_{global} .

Tetralin pyrolysis has been examined by many investigators for a variety of applications. Poutsma (8) has reviewed many of these mechanistic studies of gas, liquid, and supercritical tetralin pyrolysis in the 650 to 1000 K range. Based on his review, expected major products of supercritical tetralin pyrolysis are methylindane, naphthalene, and butylbenzene. The major products of tetralin pyrolysis found in the current investigation over a temperature range of 702 to 802 K at a pressure of 4.77 MPa are in excellent agreement with those expected.

Just as supercritical decalin pyrolysis differs mechanistically from gas phase decalin pyrolysis, Poutsma (8) argues that in a similar temperature range, supercritical and liquid tetralin pyrolysis appear to follow a different mechanistic pathway than does gas phase tetralin pyrolysis. For supercritical tetralin near 720 K and 4 to 10 MPa, similar to the conditions of this investigation, Poutsma argues that ring contraction (methylindane formation) dominates over dehydrogenation (naphthalene formation) and hydrogenolysis (butylbenzene formation); in contrast, Poutsma states that gaseous tetralin pyrolysis in the same temperature range appears to be dominated by dehydrogenation, then ring contraction, and finally C_2 loss to form benzocyclobutene.

To further detail the effects of pressure on C_6 - C_5 ring contraction in tetralin pyrolysis as well as other effects, a second set of experiments examined tetralin pyrolysis at a constant temperature of 761 K and a range of pressures from 1.8 to 9.9 MPa. The variation of methylindane yield with pressure was very similar to that of methylhexahydroindane in the decalin pyrolysis. Like methylhexahydroindane, methylindane formation was heavily favored at higher pressures. As discussed below, the favorable tetralin ring contraction in a supercritical or liquid environment noted by other authors and found experimentally in this investigation is consistent with a reaction mechanism incorporating caging effects to be reported.

The experimental evidence gathered for supercritical tetralin pyrolysis suggest a global activation energy of 273 kJ/mole and global pre-exponential of $10^{15.1} \text{ sec}^{-1}$ and compare well with the measured global decomposition parameters found for decalin, 276 kJ/mole and $10^{15.8} \text{ sec}^{-1}$. This result suggests that structural similarities between decalin and tetralin in the chemically active portions of the molecules may translate into some similarity in terms of reactivity.

Decane pyrolysis is mechanistically well understood. It is examined here to explore the potential application of decalin and tetralin as hydrogen donors to inhibit some pathways of pyrolytic decomposition and to afford the fuel greater thermal stability. These types of molecules can easily donate hydrogen to an unstable radical to terminate a chain or to discourage the formation of unsaturated hydrocarbons, which can lead to solid formation.

For supercritical pyrolysis of neat decane, major products were completely in accord with traditional pathways associated with conventional gas phase alkane pyrolysis. Radical β -scission forms 1-alkenes and smaller radicals. Smaller radicals may stabilize through an H-transfer reaction or an addition reaction to form an alkane. They also may isomerize (for example, the 1,5 H-shift isomerization), or undergo additional scission reactions to ultimately form an abundance of ethene and methane.

However, in striking contrast to conventional gas phase hydrocarbon pyrolysis which is dominated by the formation of light olefins, under supercritical conditions a much greater yield of alkanes is found along with reduced yields of ethene and 1-olefins. This observation is consistent with the fact that the ratio of the rates of H-abstraction to β -scission, normally much less than one, increases by a factor of around 50 over atmospheric pyrolysis at the same temperature due to the high concentrations of the supercritical fluid (at 4.5 MPa). For example, using representative rates of scission and abstraction from Allara and Shaw (1980), at 750 K and one atmosphere, $k_{\text{abstraction}}[\text{RH}]/k_{\text{scission}} = 0.04$. However, at 750 K and 4.5 MPa, supercritical conditions, $k_{\text{abstraction}}[\text{RH}]/k_{\text{scission}} = 1.7$. Thus, the comparatively high yields of alkanes in the supercritical state is entirely due to higher [RH].

Global kinetic parameters describing pure decane pyrolysis were found to be $E_A = 269$ kJ/mole with an A factor of $10^{15.1}$ sec⁻¹. This global activation energy is slightly below the activation energies of decalin or tetralin, 276 kJ/mole and 273 kJ/mole. This difference, in conjunction with a pre-exponential which was nearly equal in all cases (equal within the experimental uncertainty), suggests that decane is not quite as thermally stable as is decalin or tetralin under these conditions.

Finally, it appears that the addition of tetralin or decalin to decane resulted in a slight improvement in the thermal stability of decane, consistent with the results found by Song et al. (9)w who examined the stability of n-tetradecane with tetralin as an H-donor additive. Experiments conducted with mixtures of 10% decane in 90% decalin or 90% tetralin revealed that decane in the mixtures had conversions greater than a few percent at slightly higher temperatures than did neat decane. For example, a 30 percent conversion is reached at temperature of 770 for the neat fuel but is not reached until temperatures above 790 K in the decane/H-donor blend (Fig. 3). This result is also illustrated in the Arrhenius plot of Fig. 2. Rates of global decane decomposition were higher for neat decane than for decane in decalin or tetralin. Rates of decane decomposition in the two mixtures were nearly equal within the given experimental uncertainty.

C. References

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Figure Captions

- Fig. 1 Global decomposition kinetic parameters for supercritical decalin, tetralin, and decane decomposition.
- Fig. 2 Global decomposition kinetic parameters for supercritical neat decane, 10% decane in 90% decalin (molar), and 10% decane in 90% tetralin. Uncertainty in analyzing very low conversions at lower temperatures contributed to experimental noise. Decane is slightly more stable with the H-donors decalin and tetralin than neat.
- Fig. 3 Arrhenius plot of overall decalin pyrolysis
- Fig. 4 Possible mechanisms of the formation of some of the major products of decalin decomposition including methylhexahydroindane formation, representative β -scission pathways of alkene formation, and methylenecyclohexene formation.

Fig. 1

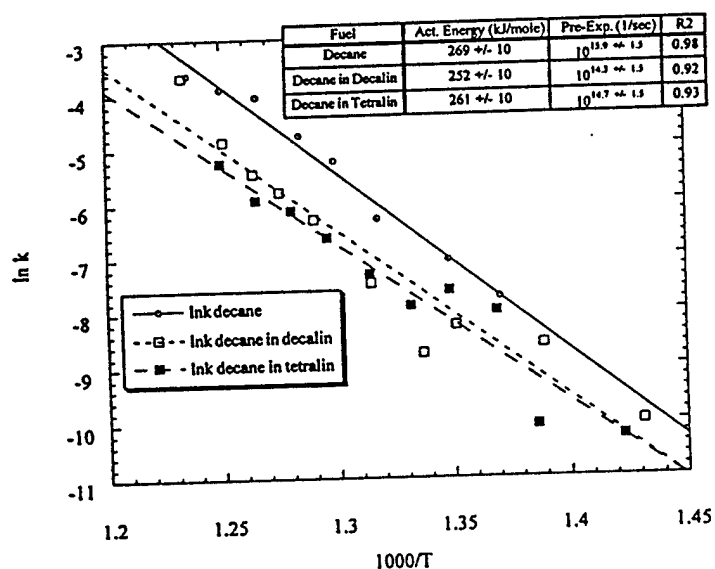
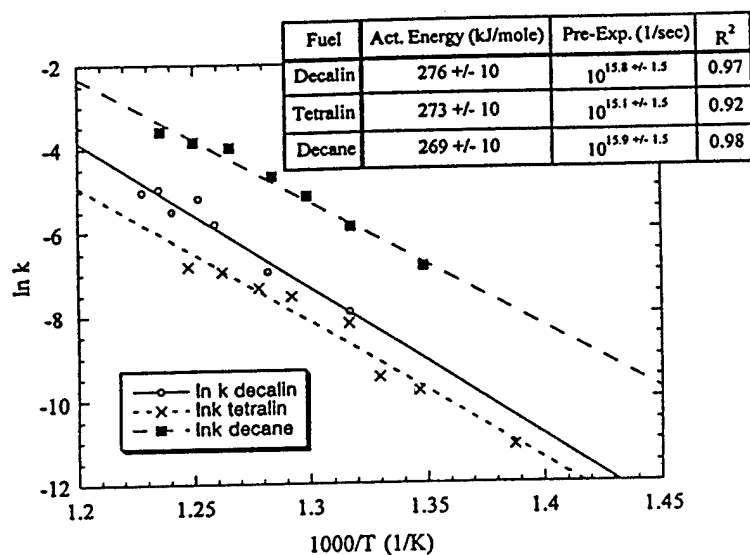


Fig. 2

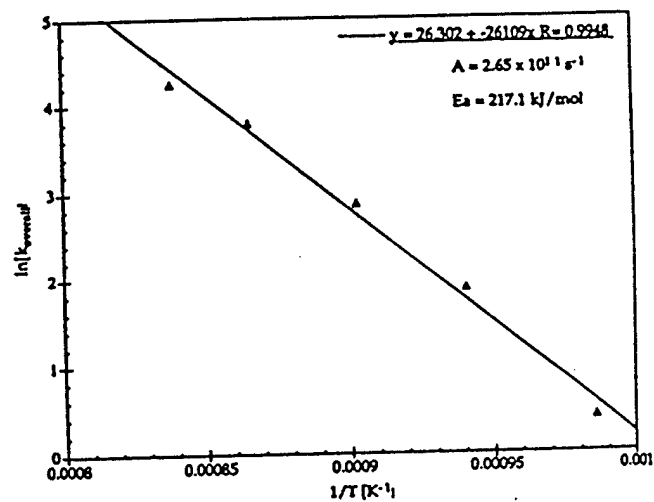
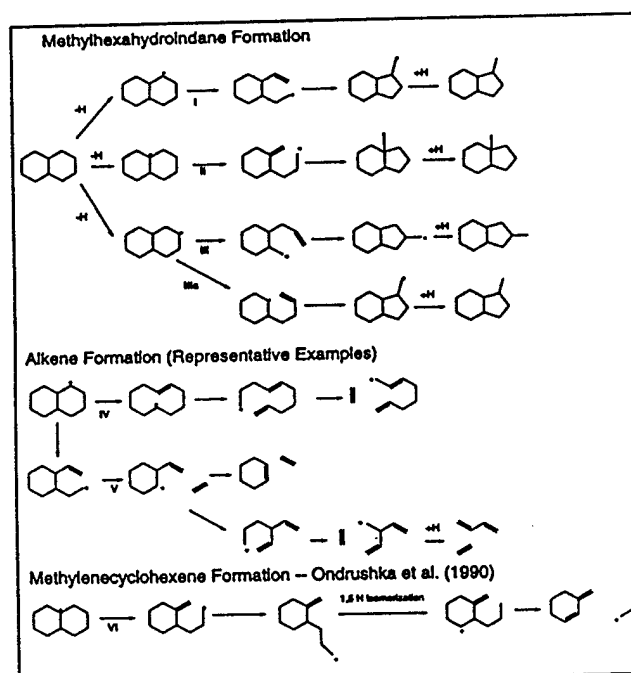


Fig. 3



Transition Under AFOSR Grant F49620-98-1-0134

Performer - I. Glassman
Customer - UTRC (Dr. M Colket)
Result - Insight into sooting problem
Application - Emissions for aircraft gas turbines

Performer - I. Glassman
Customer - Rocketdyne (Dr. R. Edelman)
Result - Sooting occurrence in rocket engines
Application - Emission from rocket engine

Performer - I. Glassman
Customer - SRI International (Dr. G. Faris)
Result - Carbon fiber formation
Application - Strong materials

Honors Award

Propellant and Combustion Award Irvin Glassman American Institute of Aeronautics and Astronautics	1998
Distinguished Teaching Award Irvin Glassman Princeton University School of Engineering and Applied Science	1998
Election to National Academy of Engineering Irvin Glassman National Academy of Engineering	1996
Ralph Coats Roe Award Irvin Glassman American Society of Engineering Education	1984
Robt. H. Goddard Professorship Irvin Glassman Princeton University	1983
Sir Alfred Egerton Gold Medal Irvin Glassman The Combustion Institute	1982

Principal Investigator Annual Data Collection (PIADC) Survey Form

PI DATA

Name Irvin Glassman

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Institution Princeton University

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NUMBER OF CONTRACT/GRANT CO-INVESTIGATORS

Faculty Post Doctorates Graduate Students Other

PUBLICATIONS RELATED TO AFOREMENTIONED CONTRACT/GRANT

Name of Journal, Book, etc.

Combustion Science and Technology

Title of Article

"Supercritical Pyrolysis of Decalin, Tetralin and n-Decane at 700-800 K. Product Distribution and Reaction Mechanism"

Authors

J. Stewart, K. Brezinsky, and I. Glassman

Publisher

V. 136, pp. 373-390, June 1998

Name of Journal, Book, etc.

27th Symposium (Int'l.) on Combustion

Title of Article

"Sooting Laminar Diffusion Flames Effect of Dilution, Additives, Pressure and Microgravity"

Authors

I. Glassman

Publisher

The Combustion Institute, Pittsburgh, PA
Accepted for publication (1998)

Name of Journal, Book, etc.

27th Symposium (Int'l.) on Combustion

Title of Article

"Modeling the Combustion of Toluene-Butane Blends"

Authors

S. Klotz, K. Brezinsky and I. Glassman

Publisher

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Name of Journal, Book, etc.

Journal of Propulsion and Power

Title of Article

"Combustion Thermodynamics of Metal-Complex Oxidizer Mixtures"

Authors

I. Glassman and P. Papas

Publisher

American Institute of Aeronautics and Astronautics
Accepted for publication (1998)

Name of Journal, Book, etc.

Journal of Physical Chemistry

Title of Article

"The Supercritical Pyrolysis of Endothermic Fuel"

Authors

J. Stewart, K. Brezinsky and I. Glassman

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Submitted 1998